శ్రీరామ   ఓం విఘ్నేశ్వరాయనమః   ఓం నమఃశివాయ

MICROWAVE SPECTROSCOPY

The spectroscopy in the microwave region is concerned with the study of rotating molecules. The three dimensional rotation of a body is quite complex and it is convenient to resolve the three dimensional rotation into rotational components about three mutually perpendicular directions through the centre of gravity. Thus a body has three principal moments of inertia and are oriented about each axis. They are designated as I_A, I_B and I_C

Basing on the values of three principal moments of inertia, molecules may be classified into groups.

1. Linear molecules: In linear molecules the atoms are arranged in straight line eg: HCl, OCS, $BeCl_2$, Acetylene etc.

In such type of molecules, the rotations may occur in three different types (i) rotation about the bond axis (ii) end-over-end rotation in the plane of the paper and (iii) end-over-end rotation at right angles to the plane. The moments of inertia about the end-over-end rotations are the same (i.e. $I_B = I_C$). The moment of inertia due to rotation about bond axis is very small and is approximated as $I_A = 0$

∴ For linear molecules $I_B = I_C$ and $I_A = 0$

2. Symmetric tops:

In symmetric top molecules, the moments of inertia about the end-over-end rotations are equal as in the case of linear molecules. But the moment of inertia due to rotation about bond axis is not negligible and is different from moments of inertia about end-over-end rotations.

For example in the molecule like methyl fluoride, the moments of inertia due to end-over-end rotations are equal i.e. $I_B = I_C$ and the moment of inertia about the bond axis is not negligible i.e. $I_A \neq 0$. Thus for symmetric top molecules $I_B = I_C \neq I_A$

$I_A \neq 0$

Now there are two possibilities i.e. $I_B = I_C > I_A$ & $I_B = I_C < I_A$. Basing on these two possibilities, the symmetric top molecules are classified into two types i.e. Prolate symmetric top molecules and oblate symmetric top molecules.

If $I_B = I_C > I_A$ then the molecules are called as prolate symmetric top molecules. Eg: Methyl fluoride.

If $I_B = I_C < I_A$ then the molecules are called as oblate symmetric top molecules. Eg: BCl_3 and in BCl_3 molecule $I_A = 2I_B = 2I_C$

(3) Spherical tops: The molecules in which, the three moments of inertia are identical are called as spherical top molecules.

Eg: In methane, all the three moments of inertia are equal.

i.e. $I_A = I_B = I_C$

(4) Asymmetric tops: The molecules in which, the three moments of inertia are different, are called as asymmetric top molecules.

$$I_A \neq I_B \neq I_C$$

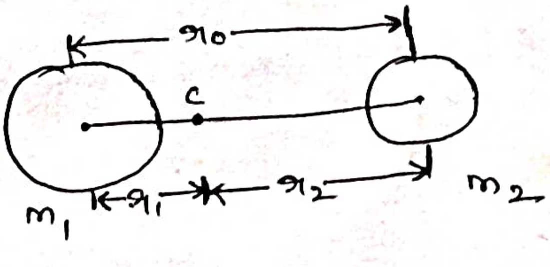
Examples: H_2O, Vinyl chloride ($CH_2=CHCl$)

Rotational Spectra:

The rotational energy of a molecule is quantized which means that a molecule cannot have any arbitrary amount of rotational energy. But the energy of the molecule is limited to certain definite values. The permitted energy values can be calculated for any molecule by solving the Schrodinger equation for the system.

Rigid diatomic molecule:

Let us consider the simplest case of linear diatomic molecule. Let us suppose that the masses m_1 and m_2 are joined by a rigid bar whose length is r_0



The length $r_0 = r_1 + r_2$ —— ①

The end-over-end rotations of the molecule occur about the point 'c' which is the centre of gravity —— ②

$$\therefore m_1 r_1 = m_2 r_2$$

The moment of inertia about 'c' is defined by

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{—— ③}$$

$r_1 = \frac{m_2 r_2}{m_1}$ —— ④ [$\because$ from equation ②]

Substituting ④ in ①

$$r_0 = \frac{m_2 r_2}{m_1} + r_2 \Rightarrow r_0 = \frac{m_2 r_2 + m_1 r_2}{m_1}$$

$$\Rightarrow m_1 r_0 = (m_1 + m_2) r_2 \Rightarrow r_2 = \frac{m_1 r_0}{m_1 + m_2}$$ —— ⑤

Similarly $r_1 = \frac{m_2 r_0}{m_1 + m_2}$ —— ⑥

Substitute the value of r_1 and r_2 in ③

$$I = m_1 \left(\frac{m_2 r_0}{m_1 + m_2}\right)^2 + m_2 \left(\frac{m_1 r_0}{m_1 + m_2}\right)^2$$

$$\Rightarrow I = \frac{m_1 m_2^2 r_0^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r_0^2}{(m_1 + m_2)^2}$$

$$\Rightarrow I = \frac{m_1 m_2 r_0^2 \cancel{(m_1 + m_2)}}{(m_1 + m_2)^{\cancel{2}}} \Rightarrow I = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$$\Rightarrow I = \mu r_0^2$$ —— ⑦

Where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and is called reduced mass of the system.

The rotational energy levels of the rigid molecule are given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules}$$ where $J = 0, 1, 2, \ldots\ldots$ —— ①

Where h is planck's constant, I is moment of inertia, J is called the rotational quantum number.

$$\therefore \epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1}$$ —— ②

Equation ② can be written as

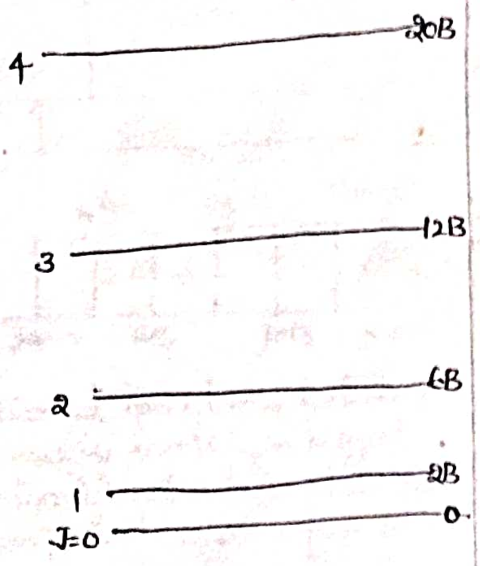
$$\epsilon_J = BJ(J+1) \text{ cm}^{-1}$$ —— ③

Where B is the rotational constant

$$B = \frac{h}{8\pi^2 Ic} \text{ cm}^{-1}$$

The energy of the allowed energy levels can be calculated using the equation③. For J=0, the energy $\epsilon_J = 0$ which means the molecule is not rotating. For J=1, the energy $\epsilon_J = 2B \text{ cm}^{-1}$. Similarly the values of ϵ_J can be calculated for increasing J values. There is no restriction on the energy of the rotating molecule. During the course of rotation of atoms in a molecule there comes a point at which the centrifugal force of the rotating molecule is greater than the strength of the bond. Hence the bond between the atoms will be broken. But this point is not reached at normal temperature. If the molecule is present in J=0 state (i.e. ground state in which no rotation occurs) and raises to J=1 state by absorbing energy from the incident radiation then the energy absorbed or the energy difference between two rotational levels J=0 and J=1 can be calculated as follows

$$\Delta\epsilon = \epsilon_{J=1} - \epsilon_{J=0}$$
$$= 2B - 0 = 2B \text{ cm}^{-1}$$



Therefore the first line in the rotational spectrum appears at 2B cm⁻¹

If the molecule raises from J=1 to J=2 state then the energy absorbed by the molecule is

$$\epsilon_{J=2} - \epsilon_{J=1} = 6B - 2B = 4B \text{ cm}^{-1}$$

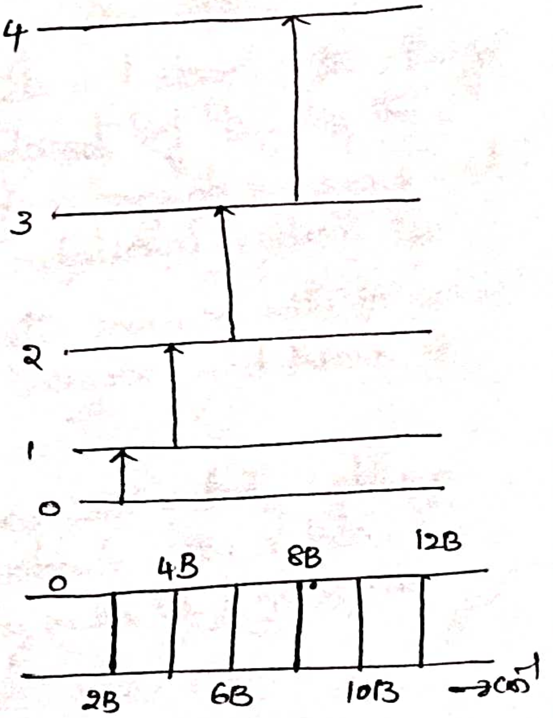
In general; if a molecule is raised from J to J+1 state then the energy absorbed by the molecule can be given by

$$\epsilon_{J+1} - \epsilon_J = B(J+1)(J+2) - BJ(J+1).$$
$$= B(J+1)\left[J+2-J\right]$$
$$= 2B(J+1) \text{ cm}^{-1}$$

All the above transitions are considered from one particular level to its immediate neighbour either above or below. The transitions like the one occurring from J=0→J=2 & from J=2→J=4 are not considered. From the sophisticated application of schrodinger equation it was found that the transitions occur between those rotational levels in which J changes by one unit, while all other transitions are spectroscopically forbidden. Such a result is called selection rule and it can be formulated as

$$\Delta J = \pm 1 \quad \text{———} \quad ④.$$

The rotational transitions in the molecule will occur only if the molecule has dipole component change. If the molecule is homonuclear then there will be no interaction between the molecule and incident radiation.



Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

Note: The microwave spectrum of a molecule is possible only if the molecule has dipole moment and exists in gaseous phase. Whereas in the solid state, molecular rotations are restricted and in the liquid state the collisions between the molecules occur too frequently to allow full rotation to occur.

Effect of Isotopic substitution:

The rotational energy of a molecule in terms of wave number is

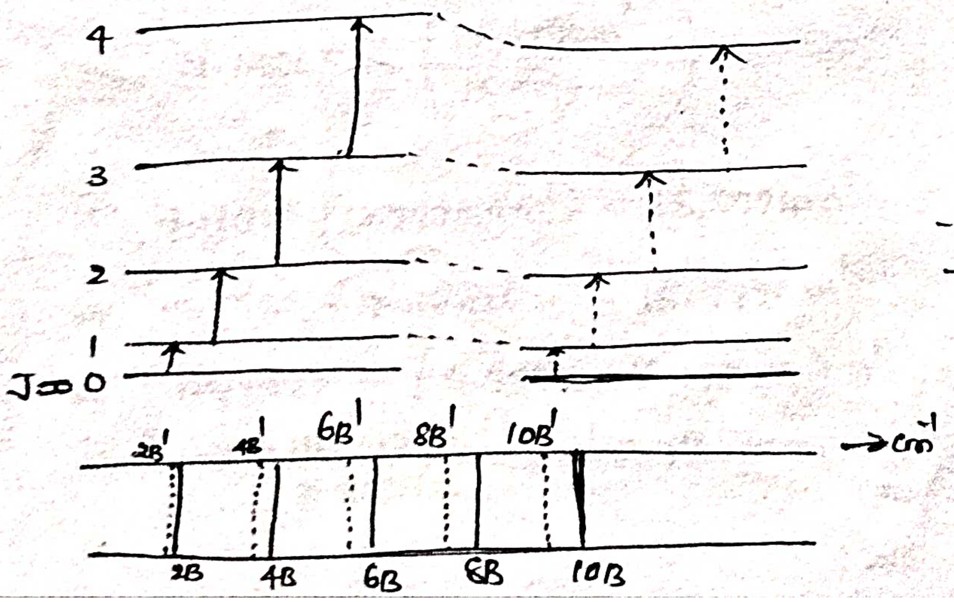
$$\epsilon_J = \frac{h}{8\pi^2 Ic} J(J+1)\ \text{cm}^{-1} \Rightarrow \epsilon_J = BJ(J+1)\ \text{cm}^{-1}$$

Where I is moment of inertia
c is velocity of light
J is rotational quantum number. ($J = 0, 1, 2, \ldots$)

When a particular atom in a molecule is replaced by its isotope (an element identical in every way expect for its mass) then there will be no appreciable change in internuclear distance. But, however a change will occur in the total mass, which in turn will result in the change of moment of inertia and B value for the molecule.

Consider the example of carbon monoxide and observe the change in the microwave spectrum when ^{12}C in CO is replaced by ^{13}C. By the replacement of ^{12}C by ^{13}C, the mass of the carbon monoxide increases and hence B value decreases, Let us designate the rotational constant of $^{13}C^{16}O$ as B' and B for $^{12}C^{16}O$. As the moment of inertia increases with increase in the total mass, the rotational constant value decreases and hence it can be concluded that $B > B'$

As a result of the change in rotational constant value, a change will occur in the rotational energy levels of the molecule. The relative change in the rotational energy levels due to change in the total mass can be represented diagramatically ad as follows.



The diagram represents the effect of isotopic substitution on the energy levels and rotational spectrum of diatomic molecule such as carbon monoxide.

The decreased separation in the rotational energy levels is useful in the evaluation of precise atomic weights.

For example, the first rotational absorption of $^{12}C^{16}O$ is found at 3.84235 cm^{-1} while that of $^{13}C^{16}O$ is found at 3.67337 cm^{-1}. The values of B and B' are 1.92118 cm^{-1} and 1.83669 cm^{-1} respectively.

$$\frac{B}{B'} = \frac{h}{8\pi^2 I c} \cdot \frac{8\pi^2 I' c}{h} = \frac{I'}{I} = \frac{\mu' r^2}{\mu r^2} = 1.046 \qquad \left[\because \frac{B}{B'} = 1.046\right]$$

$$\mu' = \frac{m' m_o}{m' + m_o} \quad \text{and} \quad \mu = \frac{m m_o}{m + m_o}$$

Where m_o is the mass of oxygen. m' is mass of carbon isotope and m is mass of carbon.

i.e. $m = 12.00$ $\quad m_o = 15.9994$

$$\therefore \frac{B}{B'} = \frac{\mu'}{\mu} = \left(\frac{m' m_o}{m' + m_o}\right)\left(\frac{m + m_o}{m m_o}\right)$$

$$\Rightarrow 1.046 = \left(\frac{m' \times 15.9994}{m' + 15.9994}\right)\left(\frac{12 + 15.9994}{12 \times 15.9994}\right)$$

$$\rightarrow 1.046 = \left(\frac{15.9994 m'}{15.9994 + m'}\right) 0.14583$$

$$\rightarrow 7.17245 = \left(\frac{15.9994 m'}{15.9994 + m'}\right)$$

$$\rightarrow 7.17245(15.9994 + m') = 15.9994 m'$$

$$\Rightarrow 114.755 + 7.17245 m' = 15.9994 m'$$

$$\Rightarrow 114.755 = (15.9994 - 7.17245) m'$$

$$\rightarrow m' = \frac{114.755}{8.82695} \Rightarrow m' = 13.0005$$

The atomic weight of carbon isotope is 13.0005. Microwave spectroscopic studies are not only useful for the determination of atomic weight but also useful for the estimation of isotopic abundance. The estimate of the isotopic abundance can be obtained from the comparison of absorption intensities.

Intensity of Spectral lines:

Inorder to know about the relative intensities of spectral lines, it is very necessary to have a knowledge about the relative probabilities of transitions between various energy levels. The selection rule for transition between various rotational levels is $\Delta J = \pm 1$. According to the selection rule, the transitions $J=0 \rightarrow J=1$ and $J=1 \rightarrow J=2$ are equally probable. Whereas the transitions between various rotational energy levels for which $\Delta J = \pm 2, \pm 3$ etc are forbidden.

The transitions between various rotational levels with $\Delta J = \pm 1$ are equally probable. It does not mean that all the transitions with $\Delta J = \pm 1$ will be equally intense. The intensity of spectral lines depends upon the number of molecules in each level.

The first factor which governs the population of the levels is the Boltzmann distribution. The rotational energy of the lowest level (ie $J=0$) is zero. Let N_0 be the no of molecules in $J=0$ state and N_J be the no of molecules in the higher state.

The Boltzmann distribution law is

$$\frac{N_J}{N_0} = e^{\frac{-E_J}{kT}} \Rightarrow \frac{N_J}{N_0} = e^{-[BhcJ(J+1)/kT]}$$

Where c is velocity of light in cm/sec, B is rotational constant in cm^{-1}.

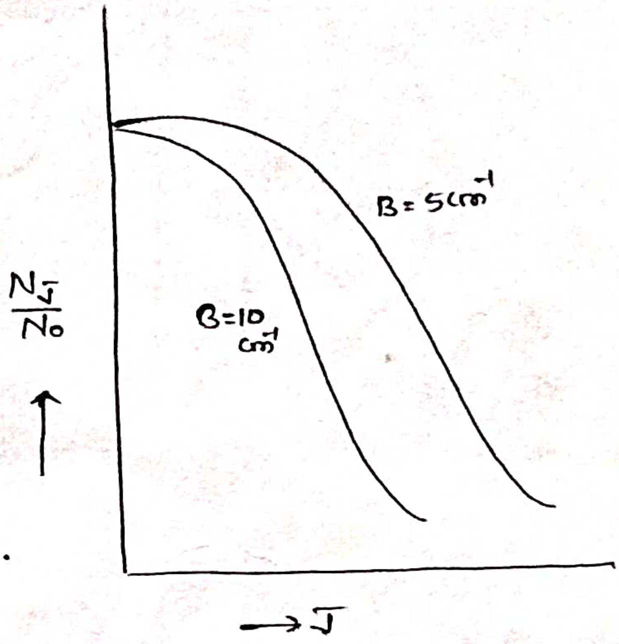
The relative population in $J=1$ state when $B = 2cm^{-1}$ and $T = 300K$ is

$$\frac{N_1}{N_0} = e^{-2(6.623\times10^{-34}\times3\times10^{10}\times1\times2)/1.38\times10^{-23}\times300}$$

$$\Rightarrow \frac{N_1}{N_0} = e^{-(0.019)} \Rightarrow \frac{N_1}{N_0} = 0.98$$

From the ratio value it is clear that, there are as many molecules in the J=1 state as in the J=0 state.

A graph is drawn taking $\frac{N_J}{N_0}$ along Y axis and rotational quantum numbers J along x-axis. The graph shows a rapid decrease of $\frac{N_J}{N_0}$ with increasing J and with larger B.



The second factor which is required to explain the intensities of spectral lines is the possibility of degeneracy in the energy states. Degeneracy is the existence of two or more states which have exactly the same energy. In case of diatomic rotor, the existence of degenerate states can be explained in terms of angular momentum.

The relation between energy and angular momentum is

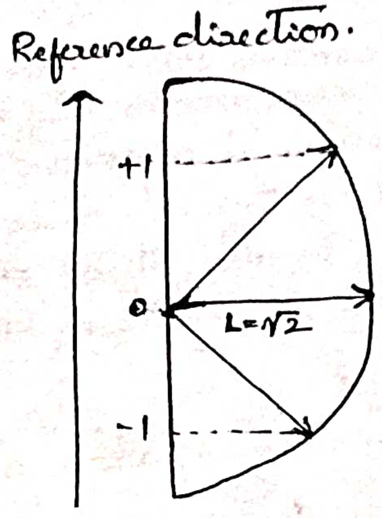
$$E=\frac{1}{2}I\omega^2 \Rightarrow E=\frac{1}{2}\frac{I^2\omega^2}{I} \Rightarrow E=\frac{L^2}{2I} \Rightarrow L^2=2EI \Rightarrow L=\sqrt{2EI}$$

$$2EI = 2\times\frac{h^2}{8\pi^2 I}J(J+1)\times I \Rightarrow 2EI=\frac{h^2}{4\pi^2}J(J+1)$$

$$\Rightarrow L=\sqrt{J(J+1)}\,\frac{h}{2\pi}$$

From the above equation we can say that angular momentum is quantised just like energy. The angular momentum L is a vector quantity. The angular momentum vector is conventionally taken to be along the direction of the axis about which the rotation occurs and it is usually drawn as an arrow of length proportional to the magnitude of the momentum. The number of different possible directions which the angular momentum vector may take up is given by quantum mechanical law.

From quantum mechanical laws, it was found that for J=1, the angular momentum vector can have only three integral or zero components along a reference direction +1, 0, −1. Thus the angular momentum vector can be oriented in three different directions with respect to the reference direction.



∴ J = 1 state is threefold degenerate

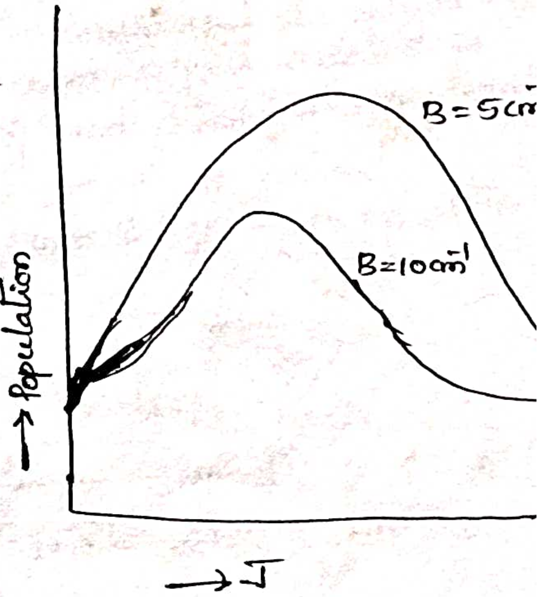
Similarly J = 2 state is fivefold degenerate and J = 3 state is seven fold degenerate.

In general each energy level is (2J+1) - fold degenerate.

The molecular population in each level decreases exponentially with increase in the J value. The degeneracy of each state increases rapidly with J. Combinedly, it can be written as

$$\text{Population} \propto (2J+1)\, e^{(-E_J/kT)}$$

When this population is plotted against J the points fall on a curve indicating that the population rises to a maximum and then diminishes



The maximum population at the nearest J value is obtained by differentiating the above equation.

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

Non-Rigid rotator:

From the rigid rotator model it can be concluded that the internuclear distance can be calculated from microwave spectra. The internuclear distance is calculated considering the first line in the rotational spectrum. If other lines were considered then a different internuclear distance ~~has~~ might have resulted as the lines would not have constant 2B separation. This pattern was clearly observed in the rotational spectrum of hydrogen fluoride. In

This spectrum the separation between the successive lines decreases steadily with increasing J. With decrease in B value, the internuclear distance increases, Hence the bond length increases with increase in J value. The assumption of a rigid bond is only an approximation. In fact all the bonds are elastic to some extent, and the increase in the length with J indicates that more quickly a diatomic molecule rotates the greater is the centrifugal force tending to move the atoms apart.

The elastic nature of the bond results in some changes which are as follows.

(i) An elastic bond may have vibrational energy.
(ii) Because of vibrational motion the quantities r and B vary.

Therefore the diatomic molecule can no more be considered as rigid and is considered to be non-rigid. When the spectrum of a non-rigid rotator is considered, the above two changes due to elastic nature of bond should be considered.

The energy for non-rigid rotator obtained from Schrodinger equation is

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \text{ Joules.} \quad ①$$

$$\therefore \epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) - \frac{h^3}{32\pi^4 I^2 r^2 k c} J^2(J+1)^2 \text{ cm}^{-1}$$

$$\rightarrow \epsilon_J = B J(J+1) - D J^2(J+1)^2 \text{ cm}^{-1} \quad ②$$

Where $B = \dfrac{h}{8\pi^2 I c}$ & $D = \dfrac{h^3}{32\pi^4 I^2 r^2 k c}$

D is centrifugal distortion constant and k is force constant

$$k = 4\pi^2 \bar{\omega}^2 \mu c^2$$

$\bar{\omega}$ is vibrational frequency expressed in cm^{-1}

Table 2.1 Rotation spectrum of hydrogen fluoride

J	$\tilde{\nu}_{obs}$† (cm^{-1})	$\tilde{\nu}_{calc}$‡ (cm^{-1})	$\Delta\tilde{\nu}_{obs}$ (cm^{-1})	B ($= \frac{1}{2}\Delta\tilde{\nu}$)	r (nm)
0	41.08	41.11			
			41.11	20.56	0.0929
1	82.19	82.18			
			40.96	20.48	0.0931
2	123.15	123.14			
			40.85	20.43	0.0932
3	164.00	163.94			
			40.62	20.31	0.0935
4	204.62	204.55			
			40.31	20.16	0.0938
5	244.93	244.89			
			40.08	20.04	0.0941
6	285.01	284.93			
			39.64	19.82	0.0946
7	324.65	324.61			
			39.28	19.64	0.0951
8	363.93	363.89			
			38.89	19.45	0.0955
9	402.82	402.70			
			38.31	19.16	0.0963
10	441.13	441.00			
			37.81	18.91	0.0969
11	478.94	478.74			

† Lines numbered according to $\tilde{\nu}_J = 2B(J+1)$ cm^{-1}. Observed data from 'An Examination of the Far Infra-red Spectrum of Hydrogen Fluoride' by A. A. Mason and A. H. Nielsen, published in Scientific Report No. 5, August 1963, Contract No. AF 19(604)-7981, by kind permission of the authors.

‡ See Sec. 2.3.5 for details of the calculation.

Generally B values have been found to be of the order of 10 cm⁻¹ and D being of the order $10^{-3}\ cm^{-1}$ [∵ K is of the order of $10^{3}\ cm^{-1}$]. Therefore for small J the correction term $DJ^2(J+1)^2$ is almost negligible, while for J = 10 or more the correction term may become appreciable.

The selection rule is same as that rigid rotor case.

i.e. $\Delta J = \pm 1$

The energy in terms of cm⁻¹ for the transition from J to J+1 state is

$$\epsilon_{J+1} - \epsilon_J = \left[B(J+1)(J+2) - D(J+1)^2(J+2)^2\right] - \left[BJ(J+1) - DJ^2(J+1)^2\right]$$

$$= B(J+1)(J+2) - BJ(J+1) - D(J+1)^2(J+2)^2 + DJ^2(J+1)^2$$

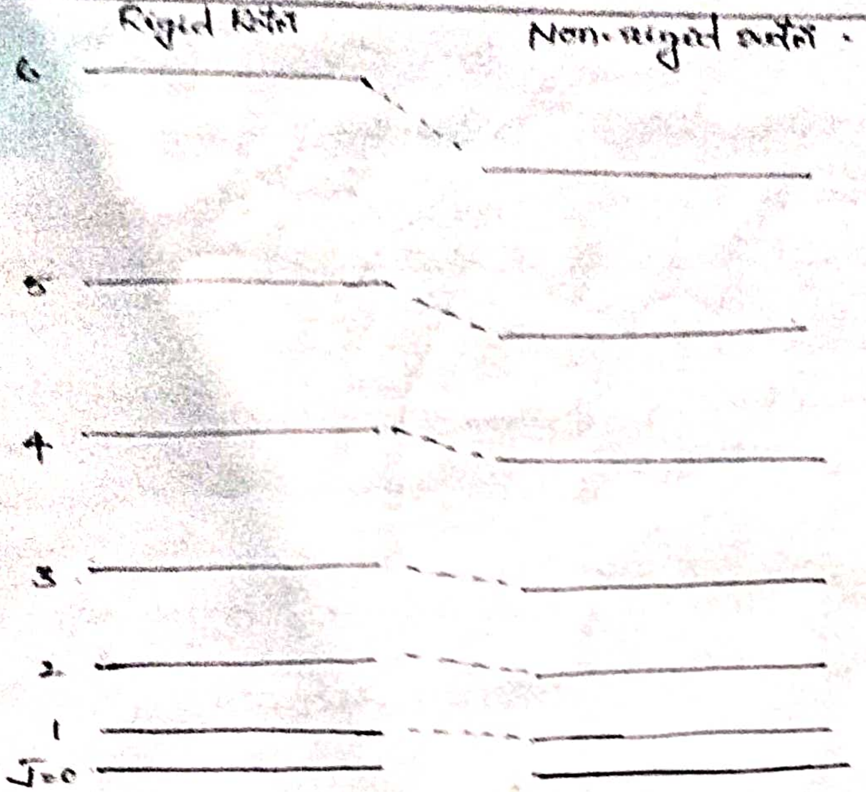
$$= B(J+1)\left[J+2-J\right] - D(J+1)^2\left[J^2+4+4J-J^2\right]$$

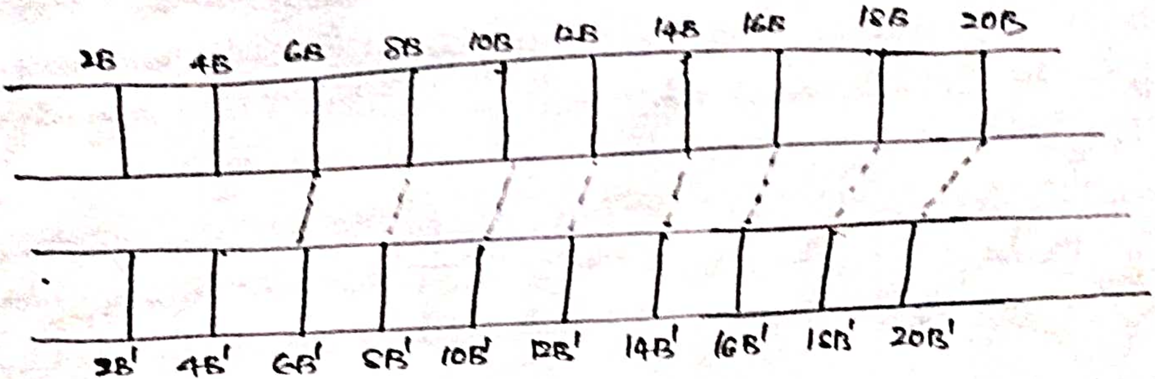
$$= 2B(J+1) - D(J+1)^2 4(J+1)$$

$$= 2B(J+1) - 4D(J+1)^3 \quad \text{———} ③$$

From equation ③ it is clear that the energy in terms of cm⁻¹ decreases for a non-rigid rotator than for a rigid rotator during the transition from J → J+1. Hence lowering of rotational levels can be observed for non-rigid rotator when compared with rigid rotator.

The value of D is useful in determining the values of $\overline{r_0}$ and to determine the J value of lines in an observed spectrum,





The above diagrams represents the rotational energy levels for rigid and non-rigid rotator and the corresponding rotational spectrum.

The relationship between D and B is

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k c} \text{ and } B = \frac{h}{8\pi^2 I c} \quad \therefore B^3 = \frac{h^3}{8^3\pi^6 I^3 c^3} \Rightarrow 16B^3 = \frac{h^3}{32\pi^6 I^3 c^3}$$

$$\rightarrow 16B^3\pi^2 = \frac{h^3}{32\pi^4 I^3 c^3} \rightarrow 16B^3\pi^2 I = \frac{h^3}{32\pi^4 I^2 c^3} \Rightarrow 16B^3\pi^2 I c^2 = \frac{h^3}{32\pi^4 I^2 c} \Rightarrow$$

$$\frac{16B^3\pi^2 I c^2}{r^2 k} = \frac{h^3}{32\pi^4 I^2 r^2 k c} \Rightarrow D = \frac{16B^3\pi^2 I c^2}{r^2 k} \rightarrow D = \frac{16B^3\pi^2 \mu r^2 c^2}{r^2 k} \rightarrow D = \frac{16B^3\pi^2\mu c^2}{k}$$

$$\Rightarrow D = \frac{16B^3\pi^2\mu c^2}{4\pi^2\omega^2\mu c^2} \rightarrow D = \frac{4B^3}{\omega^2}$$

Applications:

Linear Polyatomic molecules:

In case of linear molecules, the moments of inertia due to end-over-end rotations are equal (i.e. $I_B = I_C$) and the moment of inertia about bond axis is zero (i.e $I_A = 0$)

For example consider the linear polyatomic molecule OCS (carbonoxysulphide). The microwave spectrum of OCS is very simple as moment of inertia corresponding to end-over-end rotations are identical and moment of inertia due to rotation about bondaxis is zero.

The energy of various energy levels in general can be given by

$$\epsilon_J = BJ(J+1) - DJ^2(J+1)^2 \ldots\ldots \text{cm}^{-1} \text{\_\_\_\_\_\_\_\_ (Y)}$$

where B is rotational constant, D is centrifugal distortion constant.

The discussion about linear polyatomic molecules is similar to that of diatomic molecules, but it is necessary to consider ~~some~~ some important points.

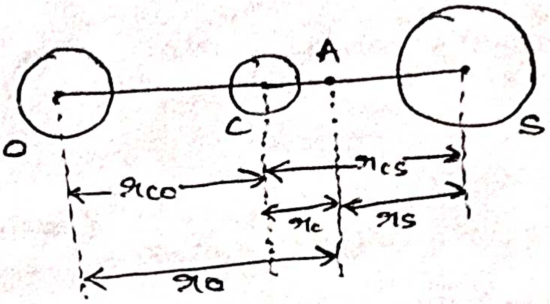
(1) The moment of inertia due to end-over-end rotation of linear polyatomic molecule is considerably greater than that of a diatomic. Hence B value is much smaller and the spectral lines in the rotational spectrum are closely placed.

(2) For the molecule to be microwave active, the molecule should possess a dipole moment. In OCS molecule there is a dipole component change and hence microwave active. Whereas for CO_2 molecule, there is no dipole component change and is microwav inactive.

(3) A non-cyclic polyatomic molecule with N atoms contains N-1 individual bonds. Thus in OCS molecule there are two bonds CO and CS with distances r_{CO} and r_{CS}. Since $I_B = I_C$ In OCS molecule, it is necessary to determine the values r_{CO} and r_{CS} one value can be the molecule has only one moment of inertia and hence only determined from the spectrum. It was observed in the rotational spectrum that all the lines are spaced at equal distance and hence we can say that there is no appreciable centrifugal distortion

To determine both r_{co} and r_{cs} we make use of isotopic substitution in the molecule as it will have different moment of inertia.

Let A be the centre of gravity of the molecule. Let r_o, r_c and r_s be the distances of oxygen, carbon and sulphur from the centre of gravity respectively. consideration of moments give



$$m_o r_o + m_c r_c = m_s r_s \quad \text{———} ②$$

The moment of inertia of the molecule can be written as

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \quad \text{———} ③.$$

$$r_o = r_{co} + r_c \text{ and } r_s = r_{cs} - r_c \quad \text{———} ④.$$

Substitute equation ④ in ② we get

$$m_o(r_{co} + r_c) + m_c r_c = m_s(r_{cs} - r_c)$$

$$\Rightarrow m_o r_{co} + m_o r_c + m_c r_c = m_s r_{cs} - m_s r_c$$

$$\Rightarrow m_o r_c + m_c r_c + m_s r_c = m_s r_{cs} - m_o r_{co}$$

$$\Rightarrow r_c(m_o + m_c + m_s) = m_s r_{cs} - m_o r_{co}$$

$$\Rightarrow M r_c = m_s r_{cs} - m_o r_{co}$$

$$\Rightarrow r_c = \left(\frac{m_s r_{cs} - m_o r_{co}}{M}\right) \quad \text{———} ⑤$$

Substituting equation ④ in ③ we get

$$I = m_o(r_{co} + r_c)^2 + m_c r_c^2 + m_s(r_{cs} - r_c)^2$$

$$= m_o(r_{co}^2 + r_c^2 + 2r_{co}r_c) + m_c r_c^2 + m_s(r_{cs}^2 + r_c^2 - 2r_{cs}r_c)$$

$$= m_o r_c^2 + m_c r_c^2 + m_s r_c^2 + m_o(r_{co}^2 + 2r_{co}r_c) + m_s(r_{cs}^2 - 2r_{cs}r_c)$$

$$= (m_o + m_c + m_s)r_c^2 + 2r_c(m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2$$

$$I = M r_c^2 + 2r_c(m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2 \quad \text{———} ⑥$$

Substituting equation ⑤ in ⑥

$$I = M\frac{(m_S r_{CS} - m_O r_{CO})^2}{M^2} + 2\left(\frac{m_S r_{CS} - m_O r_{CO}}{M}\right)(m_O r_{CO} - m_S r_{CS}) + m_O r_{CO}^2 + m_S r_{CS}^2$$

$$\Rightarrow I = \frac{(m_S r_{CS} - m_O r_{CO})^2}{M} - 2\frac{(m_S r_{CS} - m_O r_{CO})^2}{M} + m_O r_{CO}^2 + m_S r_{CS}^2$$

$$\Rightarrow I = m_O r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_S r_{CS} - m_O r_{CO})^2}{M} \quad \text{———} ⑦$$

If oxygen in the molecule ^{16}OCS is replaced by its heavier isotope ^{18}OCS then the moment of inertia can be written as

$$I' = m_O' r_{CO}^2 + m_S r_{CS}^2 - \frac{(m_S r_{CS} - m_O' r_{CO})^2}{M'} \quad \text{———} ⑧$$

Both r_{CO} and r_{CS} can be calculated from equations ⑦ and ⑧.

Table 2.2 Microwave spectrum of carbon oxysulphide

$J \rightarrow J+1$	$\bar{\nu}_{obs.}$ (cm^{-1})	$\Delta\bar{\nu}$	B(cm^{-1})
$0 \rightarrow 1$	. . .		
		2×0.4055	0.2027
$1 \rightarrow 2$	0.8109		
		0.4054	0.2027
$2 \rightarrow 3$	1.2163		
		0.4054	0.2027
$3 \rightarrow 4$	1.6217		
		0.4054	0.2027
$4 \rightarrow 5$	2.0271		

Symmetric top molecules:

The rotational energy levels of symmetric top molecules are more complicated than those of linear molecules. In case of linear molecules, the moment of inertia about the bond axis is zero (i.e. $I_A = 0$) and the moments of inertia for end-over-end rotations are equal. (i.e. $I_B = I_C$). Hence the rotational levels of linear molecules are simple. Whereas in case of symmetric top molecules, the moments of inertia about the end-over-end rotations are equal (i.e. $I_B = I_C$) and the moment of inertia about the bond axis is not negligible (i.e. $I_A \neq 0$). Therefore the molecules possess two types of rotations about ⊥ two perpendicular axes. As a result of two types of rotations for the molecules, the rotational levels are complicated.

Thus we need two quantum numbers to describe the degree of rotation, one for I_A and one for I_B & I_C. The total angular momentum of the molecule is the sum of separate angular momenta about the two different axes. 'J' is choosen to be the total angular momentum quantum number. In case of linear molecule, the quantum number 'J' represents end-over-end rotation of molecules. Whereas in case of symmetric top molecules J represents total angular momentum and K represents the angular momentum about the top axis i.e. about the C-F bond in methyl fluoride.

Therefore J and K are the quantum numbers used to describe the rotations in symmetric top molecules. The value of K cannot exceed J, since J is the total angular momentum. Additionally K can be either positive or negative. The negative and positive values of K can be imagined to correspond with clockwise and anticlockwise rotation about the symmetry axis. (C-F axis in case of CH_3F)

Consider the case of a rigid symmetric top molecule and the corresponding rotational energy of different levels can be given as,

$$\epsilon_{J,K} = \frac{E_{JK}}{hc} = BJ(J+1) + (A-B)K^2 \ \text{cm}^{-1}$$

$$\text{Where } B = \frac{h}{8\pi^2 I_{BC}} \quad \text{and } A = \frac{h}{8\pi^2 I_{AC}}$$

In the above equation the energy depends on K^2 and hence either negative or positive values of K does not create any difference for energy i.e. it is immaterial whether the top spins clockwise or anticlockwise. For all $K > 0$, the rotational energy levels are doubly degenerate.

The selection rules for this molecule may be shown as

$\Delta J = \pm 1$ and $\Delta K = 0$.

For the transition from J to J+1, the energy required can be given as

$$\epsilon_{J+1,K} - \epsilon_{J,K} = \left[B(J+1)(J+2) + (A-B)K^2\right] - \left[BJ(J+1) + (A-B)K^2\right]$$

$$\Delta\epsilon = 2B(J+1)\ cm^{-1}$$

From the above equation it is clear that the spectrum is independent of K. Hence rotational changes about symmetry axis do not give rise to rotational spectrum. The reason for this is ~~[illegible]~~ evident, that the rotation about the symmetric axis does not change the dipolemoment perpendicular to the axis and hence rotations cannot interact with radiation,

Asymmetric top molecules:

In case of asymmetric top molecules, the moments of inertia about the three mutually perpendicular axis are different i.e. $I_A \neq I_B \neq I_C$. Hence the rotational energy levels are much more complicated. No simple general equation can be derived for such molecules and they are usually treated by approximation methods.